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# Transition metal cooperative Lewis pairs using platinum(0) diphosphine monocarbonyl complexes as a Lewis base.

Krishna Mistry,<sup>1</sup> Paul G. Pringle,<sup>1\*</sup> Hazel A. Sparkes<sup>1</sup> and Duncan F. Wass<sup>2\*</sup>

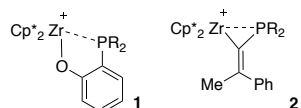
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Supporting Information available

**ABSTRACT:** The platinum(0)-diphosphine complex [Pt(CO)(L1)] (**3**, where L1 = 1,2-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>) and its diphosphinite analogue [Pt(CO)(L2)] (**11**, where L2 = 1,2-C<sub>6</sub>H<sub>4</sub>(OP<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>) act as Lewis bases in conjunction with the main group Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to form frustrated or cooperative Lewis pairs. These systems activate dihydrogen, ethene / carbon monoxide, and phenylacetylene, leading to products that depend on the exact ligand used. These subtle changes to ligand structure influence reactivity, most notably in hydrogen activation where a variety of dinuclear species of the type [(diphos)Pt(μ-H)<sub>3</sub>Pt(diphos)]<sup>+</sup> or [(diphos)Pt(μ-H)(μ-CO)Pt(diphos)]<sup>+</sup> are observed. Activation of ethene with the Lewis pair leads to a previously reported coupling product and the mechanism is probed. The basicity of [Pt(CO)(L)] is demonstrated by deprotonation of phenylacetylene. Preliminary studies with an analogous palladium complex [Pd(CO)(L1)] **33** suggests related chemistry may be exploited for this metal. These results provide further examples of cooperative Lewis pair behavior in which one of the components is based on a transition metal complex.

## INTRODUCTION

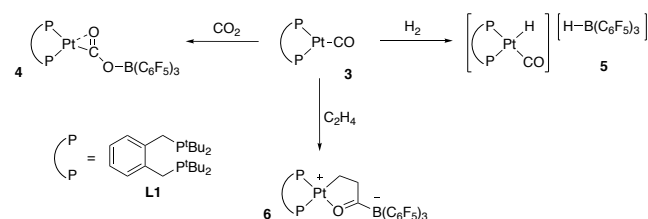
The concept of frustrated Lewis pairs (FLPs) has led to major advances in small molecule activation and catalysis by main group systems.<sup>1–7</sup> There are now many examples where activation chemistry is still observed despite a persistent interaction between Lewis acidic and basic fragments,<sup>8–11</sup> and perhaps a more accurate description of these systems would be cooperative Lewis pairs: the two Lewis centers working together to activate small molecules. Initially, FLP chemistry focused on main group compounds for the active Lewis centers. We<sup>12–16</sup> and others<sup>17–22</sup> have extended the field into the use of transition metal components as either the Lewis acid or the Lewis base (Figure 1).<sup>23</sup> We reported the intermolecular zirconocene aryloxide/phosphine, (**1**, Figure 1), which was capable of a variety of transformations including activation of H<sub>2</sub>, CO<sub>2</sub>, THF and alkyl halides.<sup>16</sup> An intermolecular variant of this system also demonstrated FLP-type reactivity, including catalytic imine hydrogenation and amine-boranes dehydrocoupling.<sup>15,24,25</sup> Erker *et al.* reported a similar intramolecular zirconocene system, (**2**, Figure 1), capable of a variety of FLP-type transformations.<sup>26</sup>



**Figure 1:** Early transition metal cooperative Lewis pairs (counterions omitted for clarity).

We were intrigued by the possibility that transition metal FLPs need not be limited to electrophilic complexes acting as the Lewis acid, and suitable electron rich, nucleophilic transition

metal complexes could act as the Lewis basic component of such a system. We have previously reported cooperative Lewis pair chemistry using the platinum(0) complex [Pt(CO)(L1)] (**3**) (L1 = 1,2-bis(di-tert-butylphosphinomethyl)benzene) as a Lewis base in conjunction with the main group Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. This system will activate carbon dioxide, dihydrogen, and ethene / carbon monoxide, leading to the expected activation products in some cases (**4** and **5**) and unprecedented reactivity in others (**6**) (Scheme 1).<sup>13</sup> Further examples of FLP-type chemistry with late transition metals have also now emerged.<sup>20–22</sup> In this present contribution, we explore a wider set of platinum(0) complexes of this family and show that subtle changes to ligand structure can have a profound influence on reactivity.

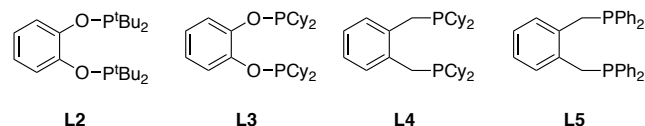


**Scheme 1:** Small molecule activation by **3**/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.

## RESULTS AND DISCUSSION

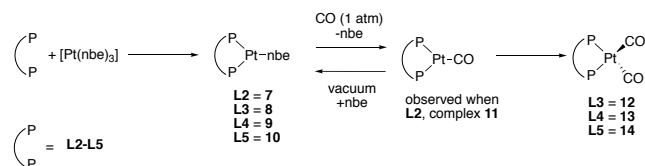
### Synthesis of [Pt(CO)(L)]

An advantage of transition metal FLPs is that steric and electronic modification can be readily achieved synthetically by simple changes to the ligand structures in sharp contrast to the often challenging syntheses associated with, for example, modified fluorinated aryl borane Lewis acids. In order to alter the electronics of the Pt(0) Lewis base, a range of related diphos ligands were synthesized **L2-L5** (Figure 2).



**Figure 2:** Series of ligands synthesized

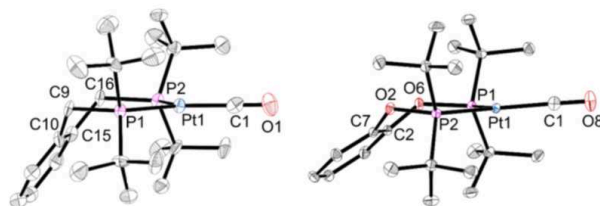
Based on the previous successful route to [Pt(CO)(**L1**)] (**3**), the general synthesis of [Pt(CO)(**L**)] started from the combination of [Pt(nbe)<sub>3</sub>] (nbe = norbornene) with the selected diphos to form mono norbornene complexes [Pt(nbe)(**L**)]<sup>13,27</sup> (Scheme 2). The coordinated nbe was displaced by bubbling CO through the reaction mixture followed by removal of the CO atmosphere, solvent and displaced nbe to form a mixture of the desired product [Pt(CO)(**L**)] and precursor [Pt(nbe)(**L**)]. These CO/vacuum cycles were repeated until full conversion of the [Pt(nbe)(**L**)] to [Pt(CO)(**L**)] was observed by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. With **L2**, the synthesis of [Pt(CO)(**L2**)] (**11**) was successful using this procedure. Unfortunately, for **L3-L5**, this sequence did not proceed smoothly; however, under a CO atmosphere, the formation of a dicarbonyl [Pt(CO)<sub>2</sub>(**L**)]<sup>27</sup> **L** = **L3-L5** is observed and confirmed by the use of <sup>13</sup>CO (see Figure S1). Removal of the CO atmosphere and the toluene solvent led to full conversion back to the starting material [Pt(nbe)(**L**)], with no evidence of the formation of [Pt(CO)(**L**)] even after several CO/vacuum cycles. Attempts to isolate the dicarbonyl complex either led to degradation or formation of [Pt(nbe)(**L**)].



**Scheme 2:** Synthesis of Pt(0) complexes of **L2-L5**.

The specific synthetic procedure to obtain complexes with diphosphine **L1** and diphosphinite **L2** varied; at least seven CO/vacuum cycles were required to achieve full conversion to the mono carbonyl complex for **L2** compared to only three cycles for **L1**. The molecular structures of [Pt(CO)(**L1**)] and [Pt(CO)(**L2**)] are shown in Figure 3. The two structures are similar and show the expected conformation of the seven membered chelates. There was no significant difference in the Pt–CO bond length in the solid state (Pt1–C1 1.853(12) and 1.8773(16) for [Pt(CO)(**L1**)] and [Pt(CO)(**L2**)] respectively) but the electronic effect of the ligand backbone is apparent when comparing the infra-red (IR) data for the carbonyl complexes. The IR stretching frequency for the carbonyl ligand in [Pt(CO)(**L2**)] ( $\nu(\text{CO}) = 1933 \text{ cm}^{-1}$ ) is significantly higher than for [Pt(CO)(**L1**)] ( $\nu(\text{CO}) = 1907 \text{ cm}^{-1}$ ). This is consistent with

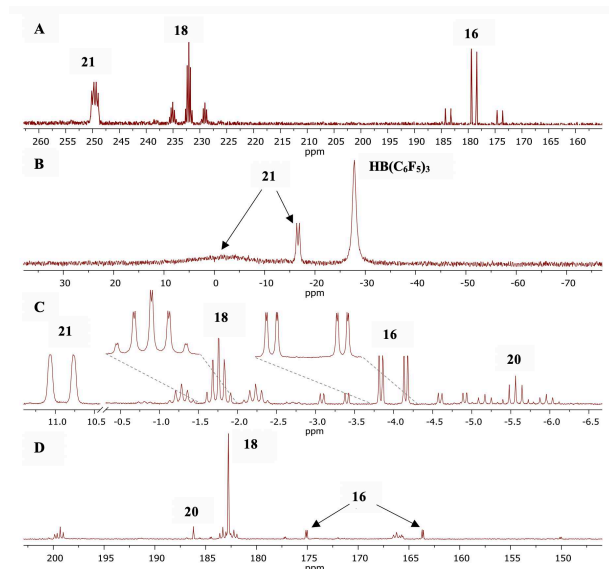
**L1** producing a more electron rich metal center than **L2** in the analogous carbonyl complexes [Pt(CO)(**L**)].



**Figure 3:** Crystal structures of [Pt(CO)(**L1**)] **3** (left) and [Pt(CO)(**L2**)] **11** (right). Thermal ellipsoids at 50%. Hydrogen atoms omitted for clarity.

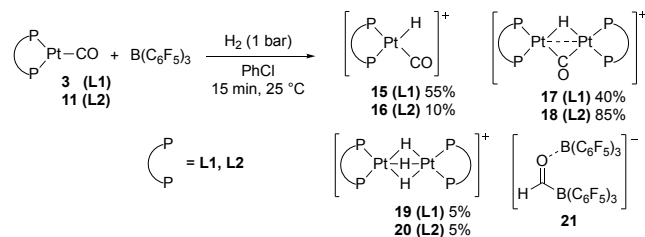
### Reaction of **11** / B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and **3** / B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with dihydrogen

Upon combination of **11** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in chlorobenzene, there was no significant change in chemical shifts in either the <sup>11</sup>B{<sup>1</sup>H} or <sup>31</sup>P{<sup>1</sup>H} NMR spectra but line-broadening was apparent for the <sup>31</sup>P{<sup>1</sup>H} NMR signal ( $w_{1/2} = 45 \text{ Hz}$ ). The solution did not change color but did exhibit thermochromic properties; upon freezing the solution in liquid nitrogen, its color changed from bright orange to a very dark purple. These observations mimic what is seen when **3** and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> are combined in chlorobenzene (line-broadening in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum and a dark green frozen solution).<sup>13</sup> The color changes indicate that some interaction between the borane and the Pt(0) complex does take place. We have previously investigated the interaction of **3** and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> by DFT calculations. It was calculated that an adduct could be formed by coordination of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to the oxygen of the CO or directly to the Pt atom in the complex.<sup>13</sup> Low temperature NMR spectroscopy studies showed sharpening of the <sup>31</sup>P{<sup>1</sup>H} NMR signal but no significant change in  $\delta_P$  or  $^1J_{PPt}$  values. Although there appears to be some interaction between the Lewis acid and the Lewis base, the evidence suggests that this interaction is weak and dynamic in solution. Since similar interactions in the **3**/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> system did not inhibit small molecule activation, further studies on the reactivity of **11** were carried out.



**Figure 4:** *In situ*  $^{13}\text{C}\{^1\text{H}\}$  (A),  $^{11}\text{B}\{^1\text{H}\}$  (B),  $^1\text{H}$  (C) and  $^{31}\text{P}\{^1\text{H}\}$  (D) NMR spectra of the reaction between **11**\*/ $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{H}_2$  after 15 min. Expansions in C show the  $^1\text{H}$ - $^{13}\text{C}$  splitting. D shows  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of reaction using **11**.

The reaction of **11**/ $\text{B}(\text{C}_6\text{F}_5)_3$  with dihydrogen resulted in a color change of the mixture from orange to bright pink within 15 min. To facilitate study by NMR spectroscopy, the reaction was repeated with  $[\text{Pt}(\text{CO})(\text{L}2)]$  (**11**\*). The reaction mixture was analyzed by *in situ*  $^1\text{H}$ ,  $^{11}\text{B}\{^1\text{H}\}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. After 15 min, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum showed the presence of three  $^{13}\text{C}$ -enriched products (Figure 4, A). The signal at  $\delta_{\text{C}} = 249.2$  ppm appeared to be a broad 1:1:1:1 quartet with a coupling constant  $^1J_{\text{CB}} = 49.3$  Hz, indicating it was directly bonded to boron. This was confirmed in the  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum (Figure 4, B) which showed a doublet at  $\delta_{\text{B}} = -16.7$  ppm ( $^1J_{\text{BC}} = 49$  Hz). When using **11**\*, a proton signal at  $\delta_{\text{H}} = 10.80$  ppm in the  $^1\text{H}$  NMR spectrum (Figure 4, C) then exhibited a  $^1J$  coupling to  $^{13}\text{C}$  ( $^1J_{\text{HC}} = 151$  Hz). This product was assigned to formyl borate anion **21** (Scheme 3). This species has been previously reported by Stephan *et al.* whilst investigating the reaction of syngas (50:50  $\text{CO}/\text{H}_2$ ) with the main group FLP,  $\text{P}^t\text{Bu}_3/\text{B}(\text{C}_6\text{F}_5)_3$ .<sup>28</sup>



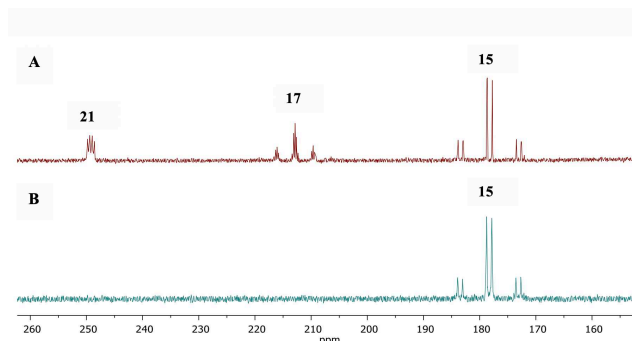
**Scheme 3:** Reaction of **3** or **11**/ $\text{B}(\text{C}_6\text{F}_5)_3$  with  $\text{H}_2$  after 15 min. Percentages of various Pt products are based on  $^1\text{H}$  NMR spectroscopic data. Ratio of **21**: $[\text{HB}(\text{C}_6\text{F}_5)_3]$  is 45:55 for **L1** and 90:10 for **L2**.

The signal at  $\delta_{\text{C}} = 178.4$  ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum corresponds to the CO ligand in the mononuclear cation **16**. The associated signals in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum occur at  $\delta_{\text{P}} =$

174.5 and 163.0 ppm (Figure 4, D) and the hydride signal in the  $^1\text{H}$  NMR spectrum at  $\delta_{\text{H}} = -4.15$  ppm (Figure 4,C).

The final signal in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum occurs at  $\delta_{\text{C}} = 231.6$  ppm and exhibits a 1:8:18:8:1 quintet of binomial quintets and corresponds to species **18**. This splitting pattern is indicative of a bridging CO ligand in a binuclear platinum species with two equivalent  $^{195}\text{Pt}$  atoms and four equivalent  $^{31}\text{P}$  atoms. The signal is a composite of three sub-spectra occurring from the different isotopic combinations of the platinum nuclei. The only isotope of Pt that is NMR active is  $^{195}\text{Pt}$  ( $I = 1/2$ ) and is 33.8% abundant; therefore there are three possible combinations of two Pt atoms in a binuclear species:  $^{195}\text{Pt}-^{195}\text{Pt}$ ,  $^{195}\text{Pt}-\text{Pt}$  and  $\text{Pt}-\text{Pt}$  (ca. 1:4:4 ratio).<sup>29</sup> The corresponding hydride signal in the  $^1\text{H}$  NMR spectrum is at  $\delta_{\text{H}} = -1.92$  ppm with the same multiplicity indicating the hydride is also bridging. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum also has the distinctive multiplicities expected for a binuclear Pt species which has been described by Otsuka for similar binuclear trihydrido species<sup>30</sup> and is also observed for analogues of **18**.<sup>31–33</sup>

The final signal in the  $^1\text{H}$  NMR spectrum at  $\delta_{\text{H}} = -5.72$  ppm (Figure 3,C) corresponds to a signal at  $\delta_{\text{P}} = 185.6$  ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (Figure 4, D) and is attributed to the trihydrido binuclear platinum species **20**; this was also confirmed by mass spectrometry. Over time, the composition of this reaction mixture did not change except for the gradual degradation of formyl borate species **21** over 4–5 days.



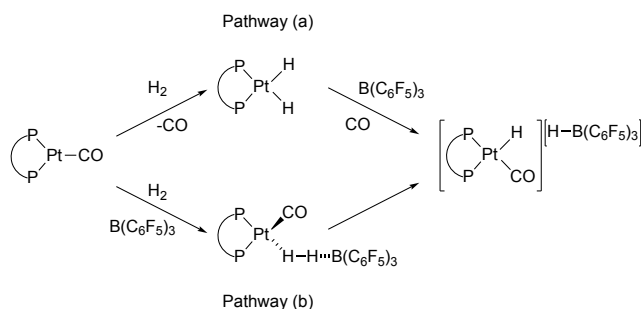
**Figure 5:** *In situ*  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the reaction between **3**\*/ $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{H}_2$  after 15 min (A) and 16 h (B).

The diversity of species observed came as a surprise, given that we have previously reported the analogous cationic species **15** and the counterion  $[\text{HB}(\text{C}_6\text{F}_5)_3]$  are the only products of dihydrogen activation with **L1** after 16 h.<sup>13</sup> The activation of dihydrogen was repeated with **3**/ $\text{B}(\text{C}_6\text{F}_5)_3$  to examine if species analogous to those derived from **11**/ $\text{B}(\text{C}_6\text{F}_5)_3$  were formed at earlier stages of the reaction. The reaction was monitored by NMR spectroscopy and after 15 min, the presence of **21**, and analogous species **15** and **17**, were detected (Figure 5, A). As previously observed, after longer periods (16 h), the NMR spectra simplified with **15** being formed as the major platinum-containing species.<sup>13</sup> There was also a trace amount ( $< 5\%$ ) of **19** detected in the  $^1\text{H}$  NMR spectrum after 15 minutes which was persistent over time.

Previously, two possible reaction pathways were proposed for dihydrogen activation by the  $\text{Pt}(0)/\text{B}(\text{C}_6\text{F}_5)_3$  Lewis pair (Scheme 4). In pathway (a), classic organometallic oxidative

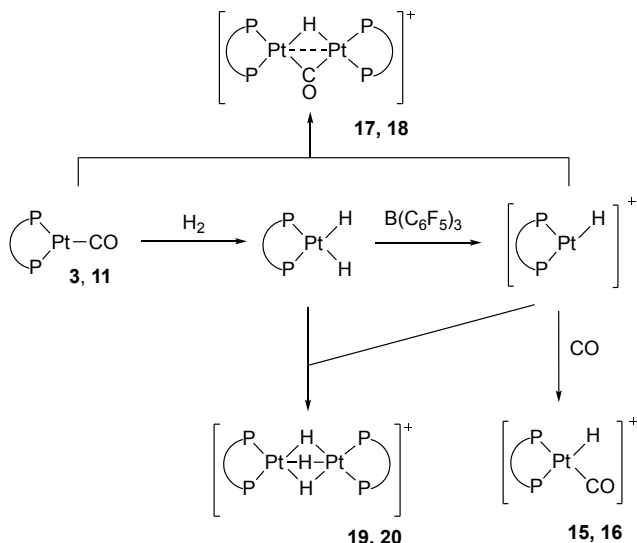


addition of H<sub>2</sub> to give the *cis*-dihydride, with loss of CO, is then followed by hydride abstraction by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and reassociation of CO. In pathway (b), the H<sub>2</sub> molecule is bound between the platinum and boron centers in an encounter complex and is then heterolytically cleaved in a concerted process to form the final dihydrogen activation products.<sup>13</sup>



**Scheme 4:** Previously proposed<sup>13</sup> pathways for dihydrogen activation by the Pt(0)/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> Lewis pair.

The starting complexes **3** or **11** do react with dihydrogen in the absence of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to form the *cis*-[Pt(H)<sub>2</sub>(L)], but this is very slow (maximum 40% conversion over 1 week) compared to the much more rapid reactions reported here; this species also reverts to [Pt(CO)(L)] when the hydrogen atmosphere is removed. There is no NMR spectroscopic evidence of the *cis*-dihydride when dihydrogen is introduced to solutions of either of the Pt(0)/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> Lewis pair systems. We previously suggested this evidence supports the more FLP-like pathway (b); however, the formation of an equilibrium with very low concentrations of the *cis*-dihydride which is then rapidly intercepted by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to pull the reaction over to the observed products via pathway (a) is also possible. Indeed, the observed complexes in this present study are neatly explained by pathway (a) (Scheme 5). Oxidative addition of H<sub>2</sub> gives the *cis*-dihydride complex with loss of CO. This species is present in low concentration but then reacts with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to abstract a hydride and form the highly reactive species [Pt(H)(L)]<sup>+</sup>. This formally 14 electron species can react with [Pt(CO)(L)] to form [Pt<sub>2</sub>(μ-H)(μ-CO)(L)<sub>2</sub>]<sup>+</sup> (**17** and **18**). Alternatively, [Pt(H)(L)]<sup>+</sup> can react with a further molecule of [Pt(H)<sub>2</sub>(L)] to give [Pt<sub>2</sub>(μ-H)<sub>3</sub>(L)<sub>2</sub>]<sup>+</sup> (**19** and **20**); this again lends support to the intermediacy of [Pt(H)<sub>2</sub>(L)]. Finally, it could also react directly by recoordination of CO to give [Pt(H)(CO)(L)]<sup>+</sup> (**15** and **16**). The ratio of these various species is linked to the stereoelectronic properties of the ligand used. The possibility of the anions [HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] or **21** being associated with any of these cationic species further adds complexity but does not detract from the main reaction sequence. Alternative pathways for the formation of binuclear species involving the concerted reaction of two platinum mono carbonyl complexes, two B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> molecules and one molecule of dihydrogen seem highly likely on the basis of the high reaction order required.

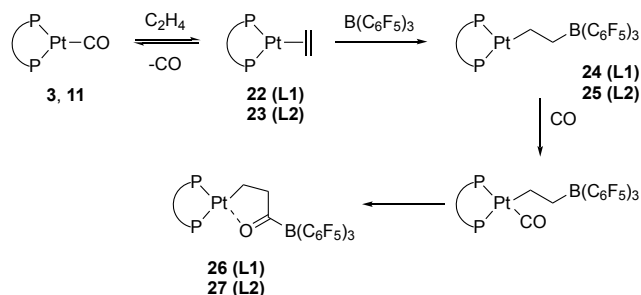


**Scheme 5:** Proposed pathways for the formation of dihydrogen activation products. Anions omitted for clarity.

It should be noted that Minghetti *et al.* have extensively studied the chemical transformation of [Pt<sub>2</sub>(μ-H)<sub>3</sub>(L)<sub>2</sub>]<sup>+</sup> to [Pt<sub>2</sub>(μ-H)(μ-CO)(L)<sub>2</sub>]<sup>+</sup> (L = dppe, 1,2-bis(diphenylphosphino)ethane) by the simple addition of CO to a solution of [Pt<sub>2</sub>(μ-H)<sub>3</sub>(L)<sub>2</sub>]<sup>+</sup>.<sup>32</sup> Studies of similar binuclear trihydrido species have shown that the structures are dynamic, with hydrido ligand exchange between bridging and terminal sites.<sup>30,31,34,35</sup> This suggests equilibria between all of the species observed here are possible.

#### Reaction of **11** / B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with ethene

The reaction of **11**/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with ethene in chlorobenzene resulted in a color change from orange to pale pink over 1 h. The reaction mixture was monitored by NMR spectroscopy; after 1 h, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum displayed two doublets at δ<sub>P</sub> = 173.4 ppm (<sup>2</sup>J<sub>PP</sub> = 15 Hz, <sup>1</sup>J<sub>PPt</sub> = 2219 Hz) and δ<sub>P</sub> = 137.5 ppm (<sup>2</sup>J<sub>PP</sub> = 15 Hz, <sup>1</sup>J<sub>PPt</sub> = 4662 Hz). Analysis of the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum showed a single sharp peak at δ<sub>B</sub> = -22 ppm indicating a 4-coordinate boron species and the <sup>1</sup>H NMR spectrum displayed two broad signals at δ<sub>H</sub> = 2.87 and 1.90 ppm. When the reaction was repeated with **11**\* a broad quartet was observed in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum at δ<sub>C</sub> = 278.7 ppm (<sup>1</sup>J<sub>CB</sub> = 52 Hz). Attempts to crystallize the product were unsuccessful but the presence of the low field signal in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum is strong evidence for the final activation product being the cyclic complex **27** (Scheme 6).

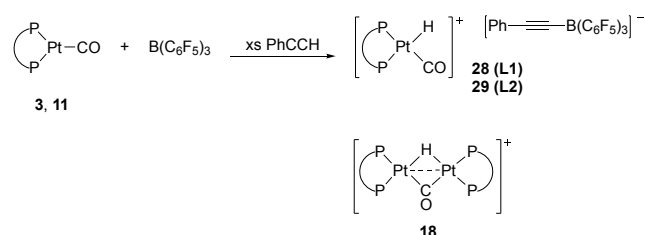


**Scheme 6:** Proposed pathway for the activation of ethene by **3** or **11**.

The **11**/ $\text{B}(\text{C}_6\text{F}_5)_3$  Lewis pair appears to have activated ethene in a similar manner to **3**/ $\text{B}(\text{C}_6\text{F}_5)_3$ , except that the rate of reaction is significantly faster, the former only taking 1 h to have detectable product signals versus 16 h for the latter. The ethene/CO coupled product **27** was also stable when the solvent and ethene atmosphere were removed and the solid residue redissolved with only minor amounts (< 3%) of decomposition.

Previous mechanistic studies would suggest an initial activation of the ethene occurs to form a product related to the structure of **24** or **25** and then further reaction with the CO to form the final product.<sup>13</sup> To investigate this, the mono ethene complex **23** was formed by subjecting **11** to at least two ethene/vacuum cycles. The formation of **23** is favorable, as after just one ethene cycle, over 95% of **11** had converted to **23**.  $\text{B}(\text{C}_6\text{F}_5)_3$  was then added to a solution of **23** in chlorobenzene and the mixture instantly turned cloudy. Addition of CO to the reaction mixture resulted in a pale pink solution with almost quantitative conversion to the ethene/CO coupled product **27**, analogous to previous observations with the formation of **26** from **3**/ $\text{B}(\text{C}_6\text{F}_5)_3$  and ethene.<sup>13</sup>

#### Reaction of $[\text{Pt}(\text{CO})(\text{L})]$ ( $\text{L} = \text{L1 or L2}$ ) / $\text{B}(\text{C}_6\text{F}_5)_3$ with phenylacetylene



**Scheme 7:** Reaction of  $[\text{Pt}(\text{CO})(\text{L})]/\text{B}(\text{C}_6\text{F}_5)_3$  with PhCCH.

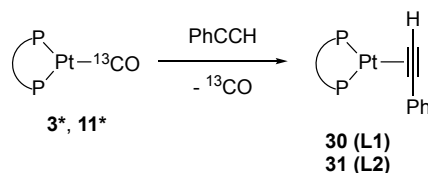
Terminal alkynes react with FLPs either by deprotonation or 1,2-addition to form an *E*-alkene.<sup>15,16,36</sup> The chemoselectivity has been found to depend predominantly on the basicity of the phosphine, although a balance of several parameters, including sterics, is necessary to control the reactivity.

The Lewis pair **3**/ $\text{B}(\text{C}_6\text{F}_5)_3$  was treated with an excess of phenylacetylene and an instant color change from bright orange to a dark red/brown was observed. After 2 h, analysis of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed full conversion of the starting material to the cationic fragment of **28** (Scheme 7). The anionic fragment has been previously reported in the literature so

assignment from the  $^{11}\text{B}\{^1\text{H}\}$  NMR and  $^{19}\text{F}$  NMR spectra was unambiguous.<sup>36</sup>

The reaction of **11**/ $\text{B}(\text{C}_6\text{F}_5)_3$  with phenylacetylene did not proceed as cleanly although the major product remains the result of deprotonation of phenylacetylene **29**. Upon addition of phenylacetylene to **11**/ $\text{B}(\text{C}_6\text{F}_5)_3$  in chlorobenzene there was an immediate color change from bright orange to dark red. Full conversion of the starting material was observed and *ca.* 90% of the product formed was assigned to complex **29** (Scheme 7). Analysis of the  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra revealed a second phosphorus-containing species, the binuclear Pt(I) cation **18**.

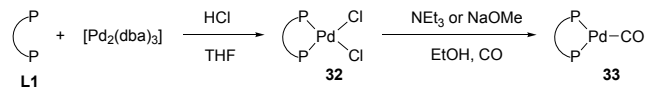
To investigate the mechanism of phenylacetylene activation for both systems, phenylacetylene was added to the **3\*** or **11\*** in the absence of  $\text{B}(\text{C}_6\text{F}_5)_3$  (Scheme 8). With **3\***, a gradual color change of the solution over 16 h from orange to pale yellow was observed. Two doublets observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (at  $\delta_{\text{P}} = 47.3$  and 42.5 ppm,  $^2J_{\text{PP}} = 24$  Hz) indicated the formation of **30**. Similar chemistry was observed with **11** ( $\delta_{\text{P}} = 190.5$  and 184.9 ppm,  $^2J_{\text{PP}} = 15.9$  Hz) although the conversion to the product **31** occurred much faster in this case (2 h). Addition of  $\text{B}(\text{C}_6\text{F}_5)_3$  to chlorobenzene solutions of **30** or **31** showed *ca.* 60% conversion to the products **28** and **29**.



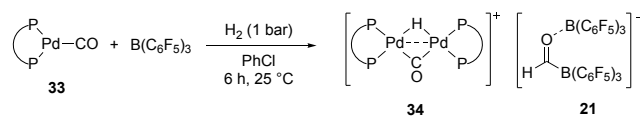
**Scheme 8:** Reaction of  $[\text{Pt}(^{13}\text{CO})(\text{L})]$  with PhCCH.

#### Synthesis and reactivity of $[\text{Pd}(\text{CO})(\text{L1})]$ (**33**) / $\text{B}(\text{C}_6\text{F}_5)_3$ pairs

The great utility of palladium complexes in catalysis made an analogous cooperative Lewis pair system based on this metal of interest. The palladium monocarbonyl complex,  $[\text{Pd}(\text{CO})(\text{L1})]$  **33** has been reported, serendipitously isolated when investigating intermediates of the methoxycarbonylation of ethene to form methyl propionate.<sup>37,38</sup> The target complex **33** was synthesised in 50% yield in two steps: firstly combining  $[\text{Pd}(\text{dba})_2]$  and **L1** in the presence of HCl to form dichlorido species  $[\text{PdCl}_2(\text{L1})]$  (**32**, Scheme 9) and then treatment with base under a CO atmosphere.



**Scheme 9:** Synthesis of  $[\text{Pd}(\text{CO})(\text{L1})]$  **33**



**Scheme 10:** Reaction of **33**/ $\text{B}(\text{C}_6\text{F}_5)_3$  with  $\text{H}_2$  in chlorobenzene at room temperature.

When **33** and  $\text{B}(\text{C}_6\text{F}_5)_3$  were combined in chlorobenzene at room temperature, an orange solution formed. No significant change in chemical shift was observed in the  $^{31}\text{P}\{^1\text{H}\}$  or  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra but broadening of the  $^{31}\text{P}\{^1\text{H}\}$  NMR signal was seen ( $w_{1/2} = 55$  Hz). When **33**/ $\text{B}(\text{C}_6\text{F}_5)_3$  was treated with  $\text{H}_2$  (1 bar), a color change from orange to yellow was observed over 6 h. Analysis of the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed quantitative conversion to a new species at  $\delta_{\text{P}} = 42.0$  ppm which appeared as a singlet. This signal corresponds to a quintet observed in the hydride region of the  $^1\text{H}$  NMR spectrum ( $\delta_{\text{H}} = -9.96$  ppm,  $^2J_{\text{HP}} = 43$  Hz, Figure S3, A). This species is tentatively assigned, from the NMR spectroscopic data, as Pd(I) species **34**, analogous to the Pt species **17** (Scheme 10). The presence of **34** was detected in positive ion ESI-MS analysis of the reaction mixture. The  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum showed a sharp signal at  $\delta_{\text{B}} = -16.2$  ppm and a broad signal at  $\delta_{\text{B}} = -2.8$  ppm and collectively with the observation of a broad singlet at  $\delta_{\text{H}} = 10.80$  ppm in the  $^1\text{H}$  NMR spectrum, the anion was confirmed to be **21** (Scheme 10). Clearly, the chemistry of this Pd system is promising but distinct from the Pt analogues and warrants further investigation.

## CONCLUSIONS

[Pt(CO)(**L2**)] (**11**) has been synthesized and compared to [Pt(CO)(**L1**)] (**3**) for cooperative Lewis pair reactivity with  $\text{B}(\text{C}_6\text{F}_5)_3$ . Whilst broadly similar reactivity is observed with substrates such as hydrogen, ethene and phenylacetylene, there are important differences. Notably, a more complex picture of bridging hydride species emerges in the hydrogen activation reactions. A new synthesis of [Pd(CO)(**L1**)] (**33**) is reported and, with  $\text{B}(\text{C}_6\text{F}_5)_3$ , this complex shows promising results for cooperative activation of hydrogen.

## EXPERIMENTAL DETAILS

### General Experimental Details

Unless otherwise stated, all reactions were carried out under an inert atmosphere ( $\text{N}_2$  or Ar) using standard Schlenk line or glovebox (MBraun  $\text{O}_2 < 0.1$  ppm,  $\text{H}_2\text{O} < 0.1$  ppm) techniques. All glassware was dried in an oven ( $200^\circ\text{C}$ ) for at least 2 hours or flame dried before use. Common laboratory solvents (DCM, diethyl ether, hexane, THF, acetonitrile and toluene) were purified using an anhydrous Grubbs-type solvent system and then degassed by at least three freeze/pump/thaw cycles. Non-standard solvents (pentane, benzene, chlorobenzene and fluorobenzene) were purchased from Sigma-Aldrich, distilled from  $\text{CaH}_2$  and degassed by at least three freeze/pump/thaw cycles. Deuterated solvents ( $\text{CDCl}_3$ ,  $\text{CD}_2\text{Cl}_2$ ,  $d_5$ -PhBr,  $d_5$ -PhCl,  $d_6$ -benzene and  $d_8$ -toluene) were obtained from commercial sources, distilled from  $\text{CaH}_2$  and degassed by at least three freeze/pump/thaw cycles. Unless otherwise stated, reagents were purchased from commercial sources and used without further purification. Reagent gases ( $\text{CO}_2$  and  $^{13}\text{CO}_2$ ) were dried prior to use by passing through a  $-78^\circ\text{C}$  trap. Catechol was dried by azeotroping with toluene three times before use. Phenylacetylene was purified by distillation before use and stored over  $4\text{ \AA}$  molecular sieves in an Ar glovebox. [Pt(norbornene)<sub>3</sub>] was synthesised according to literature method.<sup>40</sup> **3** was synthesis as reported previously.<sup>13</sup>

NMR spectra were recorded on Jeol ECS 300, Jeol ECP (Eclipse) 300, Jeol ECS 400, Bruker Nano 400, Varian VNMRs 500 and Bruker Avance III HD 500 Cryo spectrometers in the solvents stated. Chemical shifts are given in parts per million (ppm) and coupling constants ( $J$ ) are given in Hz. For paramagnetic NMR, line widths ( $w_{1/2}$ ) are given in Hz.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR chemical shifts ( $\delta$ ) are reported in parts per

million (ppm) and are referenced internally relative to the residual solvent signal.  $^{11}\text{B}\{^1\text{H}\}$ ,  $^{19}\text{F}$ ,  $^{27}\text{Al}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  were referenced to  $\text{BF}_3\cdot\text{OEt}_2$ ,  $\text{CFCl}_3$ ,  $\text{Al}(\text{NO}_3)_3$  and 85%  $\text{H}_3\text{PO}_4$  as external standards respectively. Data is reported as follows: chemical shift ( $\delta$ , ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ququ = quintet of quintets, m = multiplet, app = apparent, br = broad signal), coupling constants ( $J$ , Hz) and assignment. Electrospray Ionisation Mass spectra (ESI-MS) were recorded by the mass spectrometry service at the University of Bristol on a Bruker Daltonics microTOF II. Elemental analyses were carried out by the Microanalytical Laboratory in the School of Chemistry, University of Bristol. X-ray diffraction experiments were carried out at 100 K on a Bruker APEX II diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). The data collections were performed using a CCD area detector from a single crystal mounted on a glass fiber. Intensities were integrated, and absorption corrections based on equivalent reflections using SADABS were applied. The structures were all solved using Superflip<sup>41</sup> and structures were refined against all  $F^2$  in ShelXL2013<sup>42</sup> using Olex2.<sup>43</sup> All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were located geometrically and refined using a riding model.

### Synthesis of 1,2-bis(di-tert-butylphosphinoxy)benzene (**L2**)

Catechol (596 mg, 5.41 mmol) in THF (10 mL) was added dropwise at room temperature to a suspension of NaH (286 mg, 11.91 mmol) in THF (10 mL). Effervescence of hydrogen gas and the formation of a white suspension was observed. The reaction was left to stir at room temperature until effervescence had subsided (approx. 30 min). Di-tert-butylchlorophosphine (2.05 mL, 10.83 mmol) was added dropwise to the reaction mixture and was heated at  $60^\circ\text{C}$  for 72 h. Reaction progress was monitored by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy and upon consumption of the starting chlorophosphine the reaction mixture was filtered through celite under  $\text{N}_2$  (extra care was taken to exclude water traces). The solvent was removed *in vacuo* to yield a colourless oily solid. Recrystallisation from hexane at  $-20^\circ\text{C}$  yielded a white crystalline solid (1.38 g, 56%). Upon workup, the P–O bond hydrolysis product bond formed. After several unsuccessful attempts to isolate the pure product, the crude product was carried forward to the next step. Crystals suitable for X-ray analysis were obtained by slow evaporation of a pentane solution of **L2** at  $-40^\circ\text{C}$ .

$^1\text{H}$  NMR (400 MHz;  $\text{C}_6\text{D}_6$ )  $\delta_{\text{H}}$  7.69 (2H, m, Ar CH), 6.82 (2H, m, Ar CH), 1.21 (36H, d,  $^3J_{\text{HP}} = 11.6$  Hz,  $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz;  $\text{C}_6\text{D}_6$ )  $\delta_{\text{C}}$  150.2 (dd,  $J = 9.8, 1.7$  Hz, Ar C), 121.6 (m, Ar CH), 118.7 (d,  $J = 22.9$  Hz, Ar CH), 35.8 (d,  $J = 27.0$  Hz,  $\text{C}(\text{CH}_3)_3$ ), 27.6 (d,  $J = 15.9$  Hz,  $\text{C}(\text{CH}_3)_3$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz;  $\text{C}_6\text{D}_6$ )  $\delta_{\text{P}}$  153.1 (s,  $\text{P}(\text{Bu}_t)_2$ ); HR-MS (ESI)  $m/z$  calcd. for  $\text{C}_{22}\text{H}_{44}\text{O}_2\text{P}_2$  [ $\text{M}+\text{H}$ ] $^+$  = 399.2576, obs. 399.2568; Elem. Anal. (calcd. for  $\text{C}_{22}\text{H}_{40}\text{O}_2\text{P}_2$ ) C 66.49 (66.31), H 10.13 (10.12).

### Synthesis of 1,2-bis((dicyclohexylphosphanyl)oxy)benzene (**L3**)

Catechol (125 mg, 1.13 mmol) in THF (5 mL) was added dropwise at room temperature to a suspension of NaH (60 mg, 2.49 mmol) in THF (4 mL). A white suspension and effervescence was seen. Dicyclohexylchlorophosphine (0.5 mL, 2.26 mmol) was added to the reaction mixture dropwise. After stirring for 3 h at room temperature the reaction mixture was filtered through celite under  $\text{N}_2$  (extra care was taken to exclude water traces). The solvent was removed *in vacuo* to yield an oily solid. Recrystallisation from hexane at  $-20^\circ\text{C}$  yielded white crystals (368 mg, 65%). Crystals suitable for X-ray analysis were obtained from a saturated solution in hexane at  $-40^\circ\text{C}$ .

$^1\text{H}$  NMR (500 MHz;  $\text{C}_6\text{D}_6$ )  $\delta_{\text{H}}$  7.50 (2H, m, Ar CH), 6.84 (2H, m, Ar CH), 2.15–2.01 (4H, m, Cy  $\text{CH}_2/\text{CH}$ ), 1.88–1.53 (24H, m, Cy  $\text{CH}_2/\text{CH}$ ), 1.44–1.14 (16H, m, Cy  $\text{CH}_2/\text{CH}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz;  $\text{C}_6\text{D}_6$ )  $\delta_{\text{C}}$  150.5 (dd,  $J = 8.8, 2.1$  Hz, Ar C), 122.0 (s, Ar CH), 119.4 (d,  $J = 18.7$  Hz, Ar CH), 38.7 (d,  $J = 19.1$  Hz, Cy CH), 28.3 (d,  $J = 18.3$  Hz, Cy  $\text{CH}_2$ ), 27.5–27.2 (m, Cy  $\text{CH}_2$ ), 26.8 (d,  $J = 1.0$  Hz, Cy  $\text{CH}_2$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz;  $\text{C}_6\text{D}_6$ )  $\delta_{\text{P}}$  144.9 (s,  $\text{P}(\text{Bu}_t)_2$ ); HR-MS (ESI)  $m/z$  calcd.

for  $C_{30}H_{48}O_2P_2Na$  for  $[M+Na]^+ = 502.3130$ ; obs. = 502.3139; Elem. Anal. (calcd. for  $C_{30}H_{48}O_2P_2$ ) C 69.01 (68.77), H 8.24 (8.02).

#### Synthesis of 1,2-bis(dicyclohexylphosphino)xylene (**L4**)

KO<sup>t</sup>Bu (1.27 g, 11.3 mmol) was added to a solution of *o*-xylene (620  $\mu$ L, 5.15 mmol) in Et<sub>2</sub>O (5 mL). The white suspension was cooled to  $-78^\circ\text{C}$  and *n*-BuLi (~1.6M in hexanes, 7.4 mL, 11.8 mmol) was added dropwise whilst maintaining the temperature. The intense orange coloured solution was allowed to warm to room temperature and then refluxed for 2 h. The reaction mixture was then cooled again to  $-78^\circ\text{C}$  and a solution of ClPCy<sub>2</sub> (2.5 mL, 11.3 mmol) in Et<sub>2</sub>O (5 mL) was added dropwise and the temperature was maintained for 1 h. The reaction was warmed to room temperature and degassed H<sub>2</sub>O was added slowly. The product was extracted with DCM (4 x 8 mL) and the organic fractions combined and dried over Na<sub>2</sub>SO<sub>4</sub>. The crude product was washed with hot MeOH to yield **L4** as a white solid (934 mg, 36%). <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>)  $\delta_H$  7.14 (2H, m, Ar CH), 7.05 (2H, m, Ar CH), 3.03 (4H, br s, PCH<sub>2</sub>), 1.88-1.63 (20H, m, Cy CH<sub>2</sub>/CH), 1.57-1.47 (4H, m, Cy CH<sub>2</sub>/CH), 1.34-1.12 (20H, m, Cy CH<sub>2</sub>/CH); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; CDCl<sub>3</sub>)  $\delta_P$  -2.86 (s, P<sub>2</sub>Cy<sub>2</sub>).

#### Synthesis of 1,2-bis(diphenylphosphino)xylene (**L5**)

KPPPh<sub>2</sub> (0.5 M in THF, 5.03 mL, 2.51 mmol) was added dropwise to a solution of  $\alpha,\alpha'$ -dichloro-*o*-xylene (200 mg, 1.14 mmol) in THF (10 mL) at  $-78^\circ\text{C}$  and the reaction was stirred for 24 h at room temperature. Degassed, deionised H<sub>2</sub>O (1 mL) was added to the reaction to quench any remaining KPPPh<sub>2</sub> and the solution was passed through a silica column, washing with THF (2 x 10 mL). The volatiles were removed *in vacuo* and the product was washed with hexane (3 x 15 mL) to yield a white solid (0.319 g, 59%).

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>)  $\delta_H$  7.35-7.28 (20H, m, Ph CH), 6.90 (2H, m, Ar CH), 6.73 (2H, m, Ar CH), 3.30 (4H, s, CH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz; CDCl<sub>3</sub>)  $\delta_C$  138.4 (d, <sup>2</sup>J<sub>CP</sub> = 15.1 Hz, Ar C), 135.1 (Ar CH), 133.2 (d, <sup>1</sup>J<sub>CP</sub> = 19.1 Hz, Ph C), 130.7 (s, Ar CH), 128.8 (s, Ph-CH), 128.5 (s, Ph CH), 126.0 (s, Ph CH), 33.4 (d, <sup>1</sup>J<sub>CP</sub> = 17.4, CH<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; CDCl<sub>3</sub>)  $\delta_P$  -13.5 (s, PPh<sub>2</sub>).

#### [Pt(CO)(L2)] (**11**)

A solution of **L2** (250 mg, 0.5 mmol) in toluene (5 mL) was added dropwise to a solution of Pt(nbe)<sub>3</sub> (200 mg, 0.5 mmol) in toluene (5 mL) at  $-78^\circ\text{C}$ . After 2 h stirring at  $-78^\circ\text{C}$  a yellow suspension formed. The reaction was left to warm to room temperature and stir overnight. CO was bubbled through the suspension for 20 min during which time the reaction mixture changed to a dark orange solution. This solution was filtered to remove any Pt(0) nanoparticles. The solvent was removed *in vacuo* and the solid redissolved in toluene (5 mL). CO was bubbled through for 20 min, solvent removed *in vacuo* and redissolved in toluene (5 mL). This CO/vacuum cycle was repeated five times. The product was extracted with pentane (3 x 3 mL) and recrystallisation from this solution at  $-78^\circ\text{C}$  yielded orange crystals (164 mg, 61%). Crystals suitable for X-ray analysis were obtained from a saturated solution in pentane at  $-40^\circ\text{C}$ .

<sup>1</sup>H NMR (500 MHz; d<sub>8</sub>-toluene)  $\delta_H$  7.03 (2H, m, Ar CH), 6.69 (2H, m, Ar CH), 1.28 (36H, br d, <sup>3</sup>J<sub>HP</sub> = 14.0 Hz, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz; d<sub>8</sub>-toluene)  $\delta_C$  147.4 (m, Ar C), 128.0 (br s, Ar CH), 124.5 (br s, Ar CH), 42.4 (app t, <sup>1</sup>J<sub>CP</sub> = 5.1 Hz, <sup>2</sup>J<sub>CP</sub> = 75.3 Hz, CCH<sub>3</sub>), 29.5 (m, CCH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz; d<sub>8</sub>-toluene)  $\delta_P$  218.2 (s, <sup>1</sup>J<sub>PPt</sub> = 4062 Hz, P<sup>t</sup>Bu<sub>2</sub>); HR-MS (ESI) *m/z* calcd. for C<sub>23</sub>H<sub>41</sub>O<sub>3</sub>P<sub>2</sub>Pt [M+H]<sup>+</sup> = 622.2176, obs. 622.2169; Elem. Anal. (calcd. for C<sub>23</sub>H<sub>40</sub>O<sub>3</sub>P<sub>2</sub>Pt) C 44.81 (44.44), H 6.57 (6.49); IR  $\nu_{CO}$  1933 cm<sup>-1</sup>.

#### In situ synthesis of [Pt(<sup>13</sup>CO)<sub>2</sub>(L3)] (**12**)

A Youngs NMR tube was charged with a solution of Pt(nbe)<sub>3</sub> (13.3 mg, 0.028 mmol) and **L3** (14.0 mg, 0.028 mmol) in d<sub>8</sub>-toluene (0.7 mL). The solution was frozen in liquid nitrogen and the tube was evacuated. The solution was thawed and allowed to warm to room temperature. The tube was backfilled with <sup>13</sup>CO (1.2 bar). The solution changed from colourless to pale yellow. The product was not isolated.

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz; d<sub>8</sub>-toluene;  $-60^\circ\text{C}$ )  $\delta_C$  183.4 (t, <sup>2</sup>J<sub>CP</sub> = 15.7

Hz, <sup>1</sup>J<sub>CPt</sub> = 1743 Hz, Pt<sup>13</sup>CO); <sup>31</sup>P{<sup>1</sup>H} NMR (122 MHz; d<sub>8</sub>-toluene;  $-60^\circ\text{C}$ )  $\delta_P$  151.2 (t, <sup>2</sup>J<sub>CP</sub> = 15.7 Hz, <sup>1</sup>J<sub>PPt</sub> = 3569 Hz, P<sup>t</sup>Bu<sub>2</sub>).

#### In situ synthesis of [Pt(<sup>13</sup>CO)<sub>2</sub>(L4)] (**13**)

A Youngs NMR tube was charged with a solution of Pt(nbe)<sub>3</sub> (26.5 mg, 0.055 mmol) and **L4** (27.7 mg, 0.055 mmol) in d<sub>8</sub>-toluene (0.7 mL). The solution was frozen in liquid nitrogen and the tube was evacuated. The solution was thawed and allowed to warm to room temperature. The tube was backfilled with <sup>13</sup>CO (1.2 bar). The solution changed from colourless to pale yellow. The product was not isolated.

<sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz; d<sub>8</sub>-toluene;  $-60^\circ\text{C}$ )  $\delta_C$  184.1 (t, <sup>2</sup>J<sub>CP</sub> = 11.4 Hz, <sup>1</sup>J<sub>CPt</sub> = 1820 Hz, Pt-<sup>13</sup>CO); <sup>31</sup>P{<sup>1</sup>H} NMR (122 MHz; d<sub>8</sub>-toluene;  $-60^\circ\text{C}$ )  $\delta_P$  0.37 (t, <sup>2</sup>J<sub>CP</sub> = 11.3 Hz, <sup>1</sup>J<sub>PPt</sub> = 3114 Hz, P<sup>t</sup>Bu<sub>2</sub>).

#### In situ synthesis of [Pt(CO)<sub>2</sub>(L5)]

A Youngs NMR tube was charged with a solution of Pt(nbe)<sub>3</sub> (28.6 mg, 0.063 mmol) and **L5** (28.4 mg, 0.060 mmol) in d<sub>8</sub>-toluene (0.7 mL). The solution was frozen in liquid nitrogen and the tube was evacuated. The solution was thawed and allowed to warm to room temperature. The tube was backfilled with CO (1.2 bar) and the immediate formation of Pt nanoparticles was seen. The solution was filtered to yield a dark red solution. Attempts to isolate the product led to further degradation. <sup>1</sup>H NMR (400 MHz; d<sub>8</sub>-toluene)  $\delta_H$  7.63-7.51 (8H, m, Ph CH), 7.15-7.03 (12H, m, Ph CH), 6.62 (2H, m, Ar CH), 6.10 (2H, m, Ar CH), 3.62 (4H, m, CH<sub>2</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; d<sub>8</sub>-toluene)  $\delta_P$  -9.2 (br s, <sup>1</sup>J<sub>PPt</sub> = 3335 Hz, PPh<sub>2</sub>);  $\nu_{CO}$  (d<sub>8</sub>-toluene) 1997, 1953 cm<sup>-1</sup>.

#### Synthesis of [Pt(<sup>13</sup>CO)(L2)] (**11\***)

A Youngs NMR tube was charged with a solution of **11** (30.5 mg, 0.049 mmol) in d<sub>8</sub>-toluene (0.7 mL). The solution was frozen in liquid nitrogen and the tube was evacuated. The solution was thawed and allowed to warm to room temperature. The tube was backfilled with <sup>13</sup>CO (1.2 bar). The solution was mixed and left for 5 min before removing the solvent *in vacuo*. The solid was redissolved in d<sub>8</sub>-toluene. This cycle was repeated three more times to ensure majority of the <sup>12</sup>CO had been exchanged for <sup>13</sup>CO. This species was confirmed in solution by NMR spectroscopy only.

<sup>1</sup>H NMR (500 MHz; d<sub>8</sub>-toluene)  $\delta_H$  7.03 (2H, m, Ar CH), 6.69 (2H, m, Ar CH), 1.29 (36H, br d, <sup>3</sup>J<sub>HP</sub> = 14.1 Hz, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz; d<sub>8</sub>-toluene)  $\delta_C$  228.8 (t, <sup>2</sup>J<sub>CP</sub> = 56.5 Hz, <sup>1</sup>J<sub>CPt</sub> = 1964 Hz, Pt<sup>13</sup>CO), 147.4 (m, Ar C), 128.0 (br s, Ar CH), 124.5 (br s, Ar CH), 51.1 (app t, <sup>1</sup>J<sub>CP</sub> = 5.4 Hz, <sup>2</sup>J<sub>CP</sub> = 75.0 Hz, CCH<sub>3</sub>), 38.2 (m, CCH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz; d<sub>8</sub>-toluene)  $\delta_P$  218.2 (d, <sup>2</sup>J<sub>PC</sub> = 56.5 Hz, <sup>1</sup>J<sub>PPt</sub> = 4062 Hz, P<sup>t</sup>Bu<sub>2</sub>).

#### Synthesis of [Pt(<sup>13</sup>CO)(L1)] (**3\***)

A Youngs NMR tube was charged with a solution of **3** (29.6 mg, 0.048 mmol) in d<sub>8</sub>-toluene (0.7 mL). The solution was frozen in liquid nitrogen and the tube was evacuated. The solution was thawed and allowed to warm to room temperature. The tube was backfilled with <sup>13</sup>CO (1.2 bar). The solution was mixed and left for 5 min before removing the solvent *in vacuo*. The solid was redissolved in d<sub>8</sub>-toluene. This cycle was repeated three more times to ensure most of the <sup>12</sup>CO had been exchanged for <sup>13</sup>CO. This species was confirmed in solution by NMR spectroscopy only. NMR data is in agreement with literature.<sup>13</sup>

<sup>1</sup>H NMR (500 MHz; d<sub>8</sub>-toluene)  $\delta_H$  7.11 (2H, m, Ar CH), 6.91 (2H, m, Ar CH), 3.49 (2H, br, CH<sub>2</sub>), 1.22 (36H, m, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz; d<sub>8</sub>-toluene)  $\delta_C$  224.7 (t, <sup>2</sup>J<sub>CP</sub> = 44.1 Hz, <sup>1</sup>J<sub>CPt</sub> = 2095 Hz, Pt-<sup>13</sup>CO), 135.0 (m, Ar C), 130.8 (br s, Ar CH), 122.7 (br s, Ar CH), 33.9 (br, CH<sub>2</sub>), 29.4 (br s, CCH<sub>3</sub>), 26.9 (m, CCH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz; d<sub>8</sub>-toluene)  $\delta_P$  69.7 (d, <sup>2</sup>J<sub>PC</sub> = 44.1 Hz, <sup>1</sup>J<sub>PPt</sub> = 3680 Hz, P<sup>t</sup>Bu<sub>2</sub>).

#### Reaction of **11**/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with H<sub>2</sub>

A Youngs NMR tube was charged with a solution of **11** (31.0 mg, 0.050 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (25.5 mg, 0.050 mmol) in d<sub>5</sub>-chlorobenzene (0.7 mL). The orange solution was frozen in liquid nitrogen and the tube was evacuated. The solution was thawed and allowed to warm to room



temperature. The tube was backfilled with H<sub>2</sub> (1 bar) and shaken. A colour change from orange to bright pink was observed over 30 min, which intensified over time. Three cationic (**16** 10%, **18** 85%, **20** 5%) species (% within Pt-containing species) and two anionic species ([HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] 10% and **21** 90%) (% within B-containing species) were identified in solution.

**16**: <sup>1</sup>H NMR (500 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 6.99–6.77 (4H, m, Ar CH), 1.11–1.02 (36H, m, CCH<sub>3</sub>), –4.15 (1H, dd, <sup>1</sup>J<sub>HPt</sub> = 755 Hz, <sup>2</sup>J<sub>HP(trans)</sub> = 159 Hz, <sup>2</sup>J<sub>HP(cis)</sub> = 24.3 Hz, Pt-H); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz; d<sub>5</sub>-PhCl) δ<sub>P</sub> 174.5 (d, <sup>1</sup>J<sub>PPt</sub> = 3301 Hz, <sup>2</sup>J<sub>PP</sub> = 15.0 Hz, P<sup>o</sup>Bu<sub>2</sub>), 163.0 (d, <sup>1</sup>J<sub>PPt</sub> = 2294 Hz, <sup>2</sup>J<sub>PP</sub> = 15.0 Hz, P<sup>o</sup>Bu<sub>2</sub>).

**18**: <sup>1</sup>H NMR (500 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 6.99–6.77 (4H, m, Ar CH), 1.27–1.16 (36H, m, CCH<sub>3</sub>), –1.92 (1H, 1:8:18:8:1 ququ, <sup>1</sup>J<sub>HPt</sub> = 475 Hz, <sup>2</sup>J<sub>HP</sub> = 38 Hz, Pt(μ-H)Pt); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz; d<sub>5</sub>-PhCl) δ<sub>P</sub> 182.2 (m, <sup>1</sup>J<sub>PPt</sub> = 4029 Hz, <sup>2</sup>J<sub>PPt</sub> = 131 Hz, <sup>3</sup>J<sub>PP</sub> = 38 Hz, P<sup>o</sup>Bu<sub>2</sub>).

**20**: <sup>1</sup>H NMR (500 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 6.99–6.77 (4H, m, Ar CH), 1.27–1.16 (36H, m, CCH<sub>3</sub>), –5.72 (1H, 1:8:18:8:1 ququ, <sup>1</sup>J<sub>HPt</sub> = 393 Hz, <sup>2</sup>J<sub>HP</sub> = 41.3 Hz, Pt(μ-H)Pt); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz; d<sub>5</sub>-PhCl) δ<sub>P</sub> 185.6 (m, <sup>1</sup>J<sub>PPt</sub> = 3459 Hz, <sup>2</sup>J<sub>PPt</sub> = 153 Hz, <sup>3</sup>J<sub>PP</sub> = 10.1 Hz, P<sup>o</sup>Bu<sub>2</sub>).

[HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]: <sup>1</sup>H NMR (500 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 3.94 (br q, <sup>1</sup>J<sub>HB</sub> = 80.1 Hz, BH); <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz; d<sub>5</sub>-PhCl) δ<sub>B</sub> –27.7 (br s, BH); <sup>19</sup>F NMR (471 MHz; d<sub>5</sub>-PhCl) δ<sub>F</sub> –131.5 (6F, br, o-C<sub>6</sub>F<sub>5</sub>), –163.9 (3F, br, p-C<sub>6</sub>F<sub>5</sub>), –166.2 (6F, br, m-C<sub>6</sub>F<sub>5</sub>).

**21**: <sup>1</sup>H NMR (500 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 10.80 (br s, CH); <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz; d<sub>5</sub>-PhCl) δ<sub>B</sub> –2.4 (br, OB), –16.7 (br s, BCO); <sup>19</sup>F NMR (471 MHz; d<sub>5</sub>-PhCl) δ<sub>F</sub> –130.3 (6F, br, o-C<sub>6</sub>F<sub>5</sub>), –132.6 (6F, br, o-C<sub>6</sub>F<sub>5</sub>), –157.6 (3F, br, p-C<sub>6</sub>F<sub>5</sub>), –159.2 (3F, br, p-C<sub>6</sub>F<sub>5</sub>), –164.8 (6F, br, m-C<sub>6</sub>F<sub>5</sub>), –165.2 (6F, br, m-C<sub>6</sub>F<sub>5</sub>).

#### Reaction of **11**\*/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with H<sub>2</sub>

A Youngs NMR tube was charged with a solution of **11**\* (20.0 mg, 0.032 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (16.4 mg, 0.032 mmol) in d<sub>5</sub>-chlorobenzene (0.7 mL). The orange solution was frozen in liquid nitrogen and the tube was evacuated. The solution was thawed and allowed to warm to room temperature. The tube was backfilled with H<sub>2</sub> (1 bar) and shaken. A colour change from orange to a bright pink was observed over 30 min which intensified over time. <sup>13</sup>CO enriched analogues of the previous species were identified.

**16**: <sup>1</sup>H NMR (500 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 6.99–6.77 (4H, m, Ar CH), 1.11–1.02 (36H, m, CCH<sub>3</sub>), –4.15 (1H, ddd, <sup>1</sup>J<sub>HPt</sub> = 755 Hz, <sup>2</sup>J<sub>HP(trans)</sub> = 159 Hz, <sup>2</sup>J<sub>HP(cis)</sub> = 24.3 Hz, <sup>2</sup>J<sub>HC</sub> = 3.5 Hz, PtH); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz; d<sub>5</sub>-PhCl) δ<sub>C</sub> 178.4 (dd, <sup>1</sup>J<sub>CPt</sub> = 1212 Hz, <sup>2</sup>J<sub>CP</sub> = 124 Hz, <sup>2</sup>J<sub>CP</sub> = 6.2 Hz, Pt<sup>13</sup>CO); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz; d<sub>5</sub>-PhCl) δ<sub>P</sub> 174.5 (d, <sup>1</sup>J<sub>PPt</sub> = 3301 Hz, <sup>2</sup>J<sub>PP</sub> = 15.0 Hz, P<sup>o</sup>Bu<sub>2</sub>), 163.0 (d, <sup>1</sup>J<sub>PPt</sub> = 2294 Hz, <sup>2</sup>J<sub>PP</sub> = 15.0 Hz, P<sup>o</sup>Bu<sub>2</sub>).

**18**: <sup>1</sup>H NMR (500 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 6.99–6.77 (4H, m, Ar CH), 1.27–1.16 (36H, m, CCH<sub>3</sub>), –1.92 (1H, 1:8:18:8:1 ququ, <sup>1</sup>J<sub>HPt</sub> = 475 Hz, <sup>2</sup>J<sub>HP</sub> = 38 Hz, <sup>2</sup>J<sub>HP13C</sub> = 4.5 Hz, Pt(μ-H)Pt); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz; d<sub>5</sub>-PhCl) δ<sub>C</sub> 231.6 (1:8:18:8:1 ququ, <sup>1</sup>J<sub>CPt</sub> = 753 Hz, <sup>2</sup>J<sub>CP</sub> = 38 Hz, Pt(μ-<sup>13</sup>CO)Pt); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz; d<sub>5</sub>-PhCl) δ<sub>P</sub> 182.2 (m, <sup>1</sup>J<sub>PPt</sub> = 4029 Hz, <sup>2</sup>J<sub>PPt</sub> = 131 Hz, <sup>3</sup>J<sub>PP</sub> = 38 Hz, P<sup>o</sup>Bu<sub>2</sub>).

**20**: <sup>1</sup>H NMR (500 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 6.99–6.77 (4H, m, Ar CH), 1.27–1.16 (36H, m, CCH<sub>3</sub>), –5.72 (1H, 1:8:18:8:1 ququ, <sup>1</sup>J<sub>HPt</sub> = 393 Hz, <sup>2</sup>J<sub>HP</sub> = 41.3 Hz, Pt(μ-H)Pt); <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz; d<sub>5</sub>-PhCl) δ<sub>P</sub> 185.6 (m, <sup>1</sup>J<sub>PPt</sub> = 3459 Hz, <sup>2</sup>J<sub>PPt</sub> = 153 Hz, <sup>3</sup>J<sub>PP</sub> = 10.1 Hz, P<sup>o</sup>Bu<sub>2</sub>).

**21**: <sup>1</sup>H NMR (500 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 10.80 (br d, <sup>1</sup>J<sub>HC</sub> = 151 Hz, <sup>13</sup>CH<sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz; d<sub>5</sub>-PhCl) δ<sub>B</sub> –2.4 (br, OB), –16.7 (br d, <sup>1</sup>J<sub>BC</sub> = 49 Hz, B<sup>13</sup>C); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz; d<sub>5</sub>-PhCl) δ<sub>C</sub> 249.2 (br q, <sup>1</sup>J<sub>CB</sub> = 53 Hz, B<sup>13</sup>CO); <sup>19</sup>F NMR (471 MHz; d<sub>5</sub>-PhCl) δ<sub>F</sub> –130.3 (6F, br, o-C<sub>6</sub>F<sub>5</sub>), –132.6 (6F, br, o-C<sub>6</sub>F<sub>5</sub>), –157.6 (3F, br, p-C<sub>6</sub>F<sub>5</sub>), –159.2 (3F, br, p-C<sub>6</sub>F<sub>5</sub>), –164.8 (6F, br, m-C<sub>6</sub>F<sub>5</sub>), –165.2 (6F, br, m-C<sub>6</sub>F<sub>5</sub>).

#### Reaction of **3**\*/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with H<sub>2</sub>

A Youngs NMR tube was charged with a solution of [Pt(<sup>13</sup>CO)(**L1**)] (18.4 mg, 0.030 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (15.3 mg, 0.030 mmol) in d<sub>5</sub>-chlorobenzene (0.7 mL). The orange solution was frozen in liquid nitrogen and the tube was evacuated. The solution was thawed and allowed to warm to room temperature. The tube was backfilled with H<sub>2</sub> (1 bar) and shaken. A colour change from orange to a pale yellow was observed

over 16 h. Three cationic (**15** 55%, **17** 40%, **19** 5%) species (% within Pt-containing species) and two anionic species ([HB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] 55% and **21** 45%) (% within B-containing species) were identified in solution after 15 minutes.

**15**: <sup>1</sup>H NMR (500 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 7.20–7.02 (4H, m, ArCH), 3.71–3.10 (br, 4H, PCH<sub>2</sub>), 1.26–1.09 (36H, m, CCH<sub>3</sub>), –4.55 (1H, dd, <sup>1</sup>J<sub>HPt</sub> = 734 Hz, <sup>2</sup>J<sub>HP(trans)</sub> = 145 Hz, <sup>2</sup>J<sub>HP(cis)</sub> = 16 Hz, PtH); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz; d<sub>5</sub>-PhCl) δ<sub>C</sub> 178.2 (dd, <sup>1</sup>J<sub>CPt</sub> = 1305 Hz, <sup>2</sup>J<sub>CP</sub> = 113 Hz, <sup>2</sup>J<sub>CP</sub> = 8.8 Hz, Pt<sup>13</sup>CO); <sup>31</sup>P{<sup>1</sup>H} NMR (122 MHz; d<sub>5</sub>-PhCl) δ<sub>P</sub> 43.4 (d, <sup>1</sup>J<sub>PPt</sub> = 2987 Hz, <sup>2</sup>J<sub>PP</sub> = 19 Hz), 34.2 (d, <sup>1</sup>J<sub>PPt</sub> = 2004 Hz, <sup>2</sup>J<sub>PP</sub> = 19 Hz).

**17**: <sup>1</sup>H NMR (500 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 7.20–7.02 (4H, m, ArCH), 3.71–3.10 (br, 4H, PCH<sub>2</sub>), 1.08–0.93 (36H, m, CCH<sub>3</sub>), –5.75 (1H, 1:8:18:8:1 ququ, <sup>1</sup>J<sub>HPt</sub> = 496 Hz, <sup>2</sup>J<sub>HP</sub> = 35 Hz, Pt(μ-H)Pt); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz; d<sub>5</sub>-PhCl) δ<sub>C</sub> 212.88 (1:8:18:8:1 ququ, <sup>1</sup>J<sub>CPt</sub> = 805 Hz, <sup>2</sup>J<sub>CP</sub> = 33 Hz, Pt(μ-<sup>13</sup>CO)Pt); <sup>31</sup>P{<sup>1</sup>H} NMR (122 MHz; d<sub>5</sub>-PhCl) δ<sub>P</sub> 46.4 (m, <sup>1</sup>J<sub>PPt</sub> = 3755 Hz, <sup>2</sup>J<sub>PPt</sub> = 144 Hz, <sup>3</sup>J<sub>PP</sub> = 23 Hz).

**19**: <sup>1</sup>H NMR (500 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 6.99–6.77 (4H, m, ArCH), 1.27–1.16 (36H, m, CCH<sub>3</sub>), –7.48 (1H, 1:8:18:8:1 ququ, <sup>1</sup>J<sub>HPt</sub> = 393 Hz, <sup>2</sup>J<sub>HP</sub> = 41 Hz, Pt(μ-H)Pt); <sup>31</sup>P{<sup>1</sup>H} NMR (122 MHz; d<sub>5</sub>-PhCl) δ<sub>P</sub> 50.8 (br).

#### Reaction of **11**/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with C<sub>2</sub>H<sub>4</sub>

A Youngs NMR tube was charged with a solution of **11** (17.2 mg, 0.028 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (14.2 mg, 0.028 mmol) in d<sub>5</sub>-chlorobenzene (0.7 mL). The orange solution was frozen in liquid nitrogen and the tube was evacuated. The solution was thawed and allowed to warm to room temperature. The tube was backfilled with C<sub>2</sub>H<sub>4</sub> (1 bar) and shaken. A colour change from orange to pale pink was observed over 1 h. <sup>1</sup>H NMR (400 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 6.94–6.70 (4H, m, Ar CH), 2.87 (2H, br m, BCCH<sub>2</sub>), 1.90 (2H, br m, PtCH<sub>2</sub>), 1.19–1.08 (36H, m, CCH<sub>3</sub>); <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz; d<sub>5</sub>-PhCl) δ<sub>B</sub> –22.0 (br s, CB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>); <sup>19</sup>F NMR (376 MHz; d<sub>5</sub>-PhCl) δ<sub>F</sub> –137.2 (6F, br, o-C<sub>6</sub>F<sub>5</sub>), –167.1 (3F, br, p-C<sub>6</sub>F<sub>5</sub>), –172.1 (6F, br, m-C<sub>6</sub>F<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; d<sub>5</sub>-PhCl) δ<sub>P</sub> 173.4 (d, <sup>1</sup>J<sub>PPt</sub> = 2219 Hz, <sup>2</sup>J<sub>PP</sub> = 15.0 Hz, P<sup>o</sup>Bu<sub>2</sub>), 137.5 (d, <sup>1</sup>J<sub>PPt</sub> = 4662 Hz, <sup>2</sup>J<sub>PP</sub> = 15.0 Hz, P<sup>o</sup>Bu<sub>2</sub>).

#### Reaction of **11**\*/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with C<sub>2</sub>H<sub>4</sub>

A Youngs NMR tube was charged with a solution of **11**\* (15.8 mg, 0.025 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (13.0 mg, 0.025 mmol) in d<sub>5</sub>-chlorobenzene (0.7 mL). The orange solution was frozen in liquid nitrogen and the tube was evacuated. The solution was allowed to warm to room temperature. The tube was backfilled with C<sub>2</sub>H<sub>4</sub> (1 bar) and shaken. A color change from orange to pale pink was observed over 1 h.

<sup>1</sup>H NMR (400 MHz; d<sub>5</sub>-PhCl) δ<sub>H</sub> 6.94–6.70 (4H, m, Ar CH), 2.87 (2H, br m, BCCH<sub>2</sub>), 1.90 (2H, br m, PtCH<sub>2</sub>), 1.19–1.08 (36H, m, CCH<sub>3</sub>); <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz; d<sub>5</sub>-PhCl) δ<sub>B</sub> –22.0 (br d, <sup>1</sup>J<sub>BC</sub> = 52.4 Hz, <sup>13</sup>CB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz; d<sub>5</sub>-PhCl) δ<sub>C</sub> 278.7 (br q, <sup>1</sup>J<sub>CB</sub> = 52.4 Hz, B<sup>13</sup>CO); <sup>19</sup>F NMR (471 MHz; d<sub>5</sub>-PhCl) δ<sub>F</sub> –137.2 (6F, br, o-C<sub>6</sub>F<sub>5</sub>), –167.1 (3F, br, p-C<sub>6</sub>F<sub>5</sub>), –172.1 (6F, br, m-C<sub>6</sub>F<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; d<sub>5</sub>-PhCl) δ<sub>P</sub> 173.4 (d, <sup>1</sup>J<sub>PPt</sub> = 2219 Hz, <sup>2</sup>J<sub>PP</sub> = 15.2 Hz, P<sup>o</sup>Bu<sub>2</sub>), 137.5 (d, <sup>1</sup>J<sub>PPt</sub> = 4662 Hz, <sup>2</sup>J<sub>PP</sub> = 15.2 Hz, P<sup>o</sup>Bu<sub>2</sub>).

#### Synthesis of [Pt(C<sub>2</sub>H<sub>4</sub>)(**L2**)] (**23**)

A Youngs NMR tube was charged with a solution of **11** (25.4 mg, 0.041 mmol) in d<sub>8</sub>-toluene (0.7 mL). The solution was frozen in liquid nitrogen and the tube was evacuated. The solution was thawed and allowed to warm to room temperature. The tube was backfilled with C<sub>2</sub>H<sub>4</sub> (1.2 bar). The solution was shaken and left for 5 min before removing the solvent *in vacuo*. The solid was re-dissolved in d<sub>8</sub>-toluene. This cycle was repeated twice more. This species was confirmed in solution by NMR spectroscopy only.

<sup>1</sup>H NMR (400 MHz; d<sub>8</sub>-toluene) δ<sub>H</sub> 7.06 (2H, m, Ar CH), 6.72 (2H, m, Ar CH), 2.04 (4H, m, <sup>1</sup>J<sub>HPt</sub> = 55.6 Hz), 1.29 (36H, br d, <sup>3</sup>J<sub>HP</sub> = 14.1 Hz, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz; d<sub>8</sub>-toluene) δ<sub>C</sub> 147.7 (m, Ar C), 127.3 (s, Ar CH), 124.3 (br s, Ar CH), 42.4 (m, CCH<sub>3</sub>), 29.5 (m, CCH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; d<sub>8</sub>-toluene) δ<sub>P</sub> 198.0 (s, <sup>1</sup>J<sub>PPt</sub> = 3840 Hz, P<sup>o</sup>Bu<sub>2</sub>).

### Synthesis of [Pt(PhCCH)(L1)] (30)

A Youngs NMR tube was charged with a solution of **3**\* (20.0 mg, 0.032 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (16.6 mg, 0.032 mmol) in d<sub>5</sub>-chlorobenzene (0.7 mL). Phenylacetylene was added in excess (*ca.* 30  $\mu$ L) and an instant colour change from bright orange to a dark reddish brown colour was observed. Species **30** was identified in solution.

<sup>1</sup>H NMR (400 MHz; d<sub>5</sub>-PhCl)  $\delta_{\text{H}}$  7.12–6.96 (5H, m, PhCC), 7.12–6.96 (4H, m, Ar CH), 3.73–2.90 (4H, br, PCH<sub>2</sub>), 1.04–0.91 (36H, m, CCH<sub>3</sub>), –4.15 (1H, dd, <sup>1</sup>J<sub>HPt</sub> = 755 Hz, <sup>2</sup>J<sub>HP(trans)</sub> = 159 Hz, <sup>2</sup>J<sub>HP(cis)</sub> = 24 Hz, PtH); <sup>1</sup>B{<sup>1</sup>H} NMR (128 MHz; d<sub>5</sub>-PhCl)  $\delta_{\text{B}}$  –21.1 (br s, CCB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>); <sup>19</sup>F NMR (376 MHz; d<sub>5</sub>-PhCl)  $\delta_{\text{F}}$  –138.1 (6F, br, *o*-C<sub>6</sub>F<sub>5</sub>), –170.2 (3F, br, *p*-C<sub>6</sub>F<sub>5</sub>), –173.5 (6F, br, *m*-C<sub>6</sub>F<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; d<sub>5</sub>-PhCl)  $\delta_{\text{P}}$  43.4 (d, <sup>1</sup>J<sub>PPt</sub> = 2994 Hz, <sup>2</sup>J<sub>PP</sub> = 19 Hz, P<sup>*i*</sup>Bu<sub>2</sub>), 34.2 (d, <sup>1</sup>J<sub>PPt</sub> = 2018 Hz, <sup>2</sup>J<sub>PP</sub> = 19 Hz, P<sup>*i*</sup>Bu<sub>2</sub>).

### Synthesis of [Pt(PhCCH)(L2)] (31)

A Youngs NMR tube was charged with a solution of **11**\* (20.0 mg, 0.032 mmol) and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (16.5 mg, 0.032 mmol) in d<sub>5</sub>-chlorobenzene (0.7 mL). Phenylacetylene was added in excess (*ca.* 30  $\mu$ L) and an instant colour change from bright orange to a dark red colour was observed. Species **31** was identified in solution.

<sup>1</sup>H NMR (400 MHz; d<sub>5</sub>-PhCl)  $\delta_{\text{H}}$  7.19–6.73 (5H, m, PhCC), 6.99–6.77 (4H, m, Ar CH), 1.11–1.02 (36H, m, CCH<sub>3</sub>), –4.15 (1H, dd, <sup>1</sup>J<sub>HPt</sub> = 755 Hz, <sup>2</sup>J<sub>HP(trans)</sub> = 159 Hz, <sup>2</sup>J<sub>HP(cis)</sub> = 24 Hz, Pt-H); <sup>1</sup>B{<sup>1</sup>H} NMR (128 MHz; d<sub>5</sub>-PhCl)  $\delta_{\text{B}}$  –21.1 (br s, CCB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>); <sup>19</sup>F NMR (376 MHz; d<sub>5</sub>-PhCl)  $\delta_{\text{F}}$  –138.1 (6F, br, *o*-C<sub>6</sub>F<sub>5</sub>), –170.2 (3F, br, *p*-C<sub>6</sub>F<sub>5</sub>), –173.5 (6F, br, *m*-C<sub>6</sub>F<sub>5</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; d<sub>5</sub>-PhCl)  $\delta_{\text{P}}$  174.5 (d, <sup>1</sup>J<sub>PPt</sub> = 3301 Hz, <sup>2</sup>J<sub>PP</sub> = 15.0 Hz, P<sup>*i*</sup>Bu<sub>2</sub>), 163.0 (d, <sup>1</sup>J<sub>PPt</sub> = 2294 Hz, <sup>2</sup>J<sub>PP</sub> = 15.0 Hz, P<sup>*i*</sup>Bu<sub>2</sub>).

### Synthesis of [PdCl<sub>2</sub>(L1)] (32)

Pd(dba)<sub>2</sub> (879 mg, 1.53 mmol) and **L1** (605 mg, 1.53 mmol) were combined and stirred in THF (30 mL) for 2 d at room temperature. The red-orange solution was filtered, and the solvent was removed *in vacuo*. The resulting orange-solid was dissolved in Et<sub>2</sub>O (35 mL) and HCl (2.5 mL, 1M in Et<sub>2</sub>O) was added. Over 1 h, a dark yellow precipitate had formed. The solid was isolated and washed with Et<sub>2</sub>O (3 x 30 mL) and THF (1 x 30 mL). The product was dissolved in DCM and the insoluble material was filtered off. The desired product was then isolated as a yellow solid by precipitation from a DCM solution by slow addition of Et<sub>2</sub>O (540 mg, 62%). NMR data is in agreement with literature.<sup>44</sup>

<sup>1</sup>H NMR (400 MHz; CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_{\text{H}}$  7.38 (2H, m, Ar CH), 7.22 (2H, m, Ar CH), 3.43 (4H, m, CH<sub>2</sub>), 1.60 (36 H, d, <sup>3</sup>J<sub>HP</sub> = 14.0 Hz, C(CH<sub>3</sub>)<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz; CD<sub>2</sub>Cl<sub>2</sub>)  $\delta_{\text{P}}$  37.2 (s, P<sup>*i*</sup>Bu<sub>2</sub>).

### Synthesis of [Pd(CO)(L1)] (33)

Compound **32** (100 mg, 0.17 mmol) was dissolved in EtOH (CO saturated) and then the yellow suspension was sparged with CO and kept under a CO atmosphere (CO balloon). NEt<sub>3</sub> (50  $\mu$ L, 0.35 mmol) was added and then the reaction mixture was sparged with CO. A darkening of the reaction mixture was seen, and a yellow precipitate formed in a dark orange solution. The yellow solid was isolated as the desired product (49 mg, 55%).

<sup>1</sup>H NMR (400 MHz; d<sub>8</sub>-toluene)  $\delta_{\text{H}}$  7.13 (2H, m, Ar CH), 6.90 (2H, m, Ar CH), 3.10 (4H, m, CH<sub>2</sub>), 1.21 (36H, m, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz; d<sub>8</sub>-toluene)  $\delta_{\text{C}}$  130.0 (br s, Ar CH), 122.0 (br s, Ar CH), 33.5 (br, CH<sub>2</sub>), 29.0 (br s, CCH<sub>3</sub>), 26.0 (m, CCH<sub>3</sub>) 135.0 (m, Ar C), (note: Pt-CO not observed); <sup>31</sup>P{<sup>1</sup>H} NMR (400 MHz; d<sub>8</sub>-toluene)  $\delta_{\text{P}}$  50.0 (s, P<sup>*i*</sup>Bu<sub>2</sub>); IR  $\nu_{\text{CO}}$  1955 cm<sup>–1</sup>.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Selected NMR spectra. Crystallographic details for **2**, **3** and **11** (cif files)

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The platinum(0) complex [Pt(CO)(L1)] **3** (L1 = 1,2-bis(di-tert-butylphosphinomethyl)benzene) and its diphosphinite analogue [Pt(CO)(L2)] **11** act as Lewis bases in conjunction with the main group Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to form cooperative Lewis pairs, capable of activating a range of small molecules including hydrogen, ethene and phenylacetylene.

